

Poly(crystal violet)/graphene-modified electrode for the simultaneous determination of trace lead and cadmium ions in water samples

Meifeng Chen · Mingyong Chao · Xinying Ma

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Abstract A novel poly(crystal violet)/graphene-modified glassy carbon electrode (PCV/Gr/GCE) was fabricated for the simultaneous determination of Pb^{2+} and Cd^{2+} . The electrochemical behavior of both species at the PCV/Gr/GCE was investigated employing cyclic voltammetry. In acetate buffer, the modified electrode showed an excellent electrocatalytical effect on the oxidation of both species and was further used for their determination. Under optimized analytical conditions, the oxidation peak currents of Pb^{2+} and Cd^{2+} obtained by differential pulse voltammetry in pH 4.6 acetate buffer showed a linear relationship with their concentrations in the ranges of 2.00×10^{-8} – $1.95 \times 10^{-5} \text{ mol L}^{-1}$ and 4.00×10^{-8} – $5.58 \times 10^{-5} \text{ mol L}^{-1}$, respectively. The developed method has excellent sensitivity, selectivity, reproducibility and has been successfully applied to the determination of Pb^{2+} and Cd^{2+} in water samples.

Keywords Poly(crystal violet)/graphene-modified electrode · Lead and cadmium · Cyclic voltammetry · Differential pulse voltammetry

1 Introduction

Heavy metal pollution is becoming more and more serious in many regions of the world due to emission from mining, discharge of waste gases, discard of batteries, etc. [1]. These metals are nonbiodegradable and can accumulate in the food chain, posing a great danger to animals and human

beings [2]. Lead and cadmium are among the major heavy metal pollutants found in both terrestrial and aquatic ecosystems [1, 3, 4]. Lead and cadmium are genotoxic and can affect directly or indirectly to biota and human being [3, 5], and their environmental contamination has become a general concern across the world, which leads to the increasing need for their determination in a variety of matrices. Voltammetry is an effective technique for the determination of trace amounts of metal ions due to its convenience, fastness, high sensitivity, selectivity, and reproducibility [6–11]. Many voltammetric methods using various modified electrodes have been developed for the simultaneous determination of Pb^{2+} and Cd^{2+} . Among these methods, stripping voltammetric methods using modified electrodes with various mercury-based modifiers were mostly reported and exhibited great sensitivity [12–23]; however, the toxicity of mercury causes a great limitation to the practical application of these methods. To replace the toxic and volatile mercury, nontoxic bismuth was used to fabricate a variety of solid electrodes using bismuth-based modifiers [6, 24–34]. Recently, a number of other modified electrodes with modifiers such as graphene [35], titanium dioxide/zirconium dioxide [36], carbon nanotubes [37, 38], montmorillonite-calcium [39], conductive polyaniline [40] were reported. Although a lot of electrochemical methods for the simultaneous determination of Pb^{2+} and Cd^{2+} have been proposed, with the development of new sensor technology and due to the great significance of heavy metal determination, many researchers are still working in this field and striving for better methods.

Graphene, an allotrope of carbon, has attracted considerable attention in both fundamental science and applied research since its initial isolation from graphite crystals in 2004 [41]. Its unique properties such as good electrical

M. Chen · M. Chao (✉) · X. Ma
Department of Chemistry and Chemical Engineering, Heze University, Heze 274015, People's Republic of China
e-mail: chaomingyong@foxmail.com

conductivity, high electron mobility, and exceptional mechanical strength make it an excellent electrode material, and a variety of graphene composite electrodes such as polyaniline/graphene-modified electrode and the CdS–graphene composite have been fabricated for electrochemical studies [42, 43]. Graphene sheets can interact supramolecularly with conjugated compounds containing benzene rings through strong π – π interactions, resulting strong adsorption and fast electron transfer rate between them [44]. Crystal violet is a family of organic compounds containing three benzene rings. When polymerized onto the surface of an electrode, it shows excellent electrocatalytic activity. The goal of the study is to fabricate a composite poly(crystal violet)/graphene electrode and to investigate the synergetic catalytic effect of graphene and poly(crystal violet) toward the oxidation of lead and cadmium ions. Furthermore, this study is to establish a novel method for the simultaneous determination of trace lead and cadmium ions in water samples.

In this study, a poly(crystal violet)/graphene-modified electrode (PCV/Gr/GCE) was fabricated using a two-step procedure by electropolymerizing crystal violet onto the surface of a graphene-modified electrode, which is obtained by casting a certain amount of well-dispersed graphene suspension onto a prior polished glassy carbon electrode. Using the fabricated PCV/Gr/GCE, an electrochemical sensor for the simultaneous determination of Pb^{2+} and Cd^{2+} was developed, and the electrochemical behavior of the two species at the PCV/Gr/GCE were investigated. Experimental results showed that the composite film of graphene and poly(crystal violet) exhibited excellent electrocatalytic activity toward the oxidation of Pb^{2+} and Cd^{2+} , giving clear increases in their oxidation currents. The oxidation peak current of Pb^{2+} showed a linear relationship with its concentration in the range of 2.00×10^{-8} – $1.95 \times 10^{-5} \text{ mol L}^{-1}$, with a detection limit of $6.00 \times 10^{-9} \text{ mol L}^{-1}$. The oxidation peak current of Cd^{2+} showed a linear relationship with its concentration in the range of 4.00×10^{-8} – $5.58 \times 10^{-5} \text{ mol L}^{-1}$, with a detection limit of $1.00 \times 10^{-8} \text{ mol L}^{-1}$. The PCV/Gr/GCE shows excellent selectivity, sensitivity, and repeatability in the detection of Pb^{2+} and Cd^{2+} and has been demonstrated by the simultaneous determination of the two species in water samples.

2 Experimental

2.1 Chemicals and reagents

Nanographene was synthesized from graphite powder according to our previously reported method [45]. Crystal violet was purchased from Guangzhou Chemical Reagent

Factory (Guangzhou, China). Pb^{2+} and Cd^{2+} standard solutions were obtained from Institute for Environmental Reference Materials of Ministry of Environmental Protection (Beijing, China). Phosphate buffer solution (pH 6.0) was prepared by mixing the stock solutions of $0.20 \text{ mol L}^{-1} \text{ Na}_2\text{HPO}_4$ and 0.10 mol L^{-1} citric acid. Acetate buffer solutions (HAc–NaAc, pH 2.6–5.8) were prepared by mixing 0.20 mol L^{-1} sodium acetate and 0.30 mol L^{-1} acetic acid. All other chemicals and reagents were of analytical grade and used as received.

2.2 Instrumentation

The bare glassy carbon electrodes (GCE, 3.00 mm in diameter) were purchased from Chen-hua, Instruments, Inc. (Shanghai, China). The voltammograms were obtained on a CHI 660C Electrochemical Workstation (Chen-hua, Shanghai, China) with a three-electrode system consisting of a working electrode (a bare GCE, a Gr/GCE, or PCV/Gr/GCE, 3.00 mm in diameter), a counter electrode (a platinum wire electrode), and a reference electrode (a Ag/AgCl electrode). Scanning electron microscope (SEM) image was obtained using a field emission SEM Sirion 200 (FEI, America). Acidity was measured with a PHS-3B Precision pH Meter (Shanghai, China), and all sonication were done using a KQ-100 Ultrasonic Cleaner (Kunshan, China).

2.3 Preparation of the graphene-modified glassy carbon electrode

Seven milligram of nanographene powder was dispersed in 10.00 mL of double distilled water with ultrasonication for 20 min to give a black graphene suspension. Prior to modification, a bare glassy carbon electrode (3.0 mm in diameter) was polished with abrasive paper (grit 2000) and wet alumina powder ($0.05 \mu\text{m}$). Then, to remove alumina particulates, the electrode was rinsed ultrasonically with 1:1 HNO_3 , absolute ethanol, and distilled water, respectively. After rinsing, the electrode was dried under infrared lamp. 5.00 μL of the graphene suspension prepared above was cast on the surface of the pretreated GCE and dried under infrared lamp to give a graphene-modified electrode.

2.4 Fabrication of PCV/Gr/GCE and PCV/GCE

Utilizing a newly prepared Gr/GCE as working electrode, a Ag/AgCl electrode as reference electrode, and a platinum as counter electrode, the poly(crystal violet)/graphene composite electrode was prepared by immersing the Gr/GCE into an aqueous solution prepared by mixing 10.00 mL of 0.20 mol L^{-1} phosphate buffer solution (pH 6.0), 6.00 mL of 0.050 mol L^{-1} potassium nitrate solution, and 4.00 mL of $1.00 \times 10^{-3} \text{ mol L}^{-1}$ crystal violet

solution and sweeps in a potential range from -1.2 to 1.8 V for 12 cycles at a scan rate of 80 mV s^{-1} without stirring; then the surface of modified electrode was washed with double distilled water and dried under infrared lamp to give a PCV/Gr/GCE. A PCV/GCE was similarly fabricated for comparison studies.

2.5 Electrochemical measurement

All electrochemical measurements were performed using a CHI 660C Electrochemical Workstation having a conventional three-electrode cell configuration comprising a bare GCE or a PCV/GCE or a PCV/Gr/GCE as the working electrode, a Ag/AgCl electrode as the reference electrode, and a platinum as the counter electrode. Prior to each measurement, cyclic scans were performed in 0.20 mol L^{-1} acetate buffer solution (pH 4.6) between -1.6 and 0.4 V until stable voltammograms that were obtained; then certain amounts of acetate buffer solution (pH 4.6) and Pb^{2+} and Cd^{2+} standard solutions were pipetted in the voltammetric cell, and cyclic voltammograms or differential pulse voltammograms were recorded at a scan rate of 100 mV s^{-1} in appropriate potential ranges. Upon completion of each measurement, the working electrode was immersed in 0.20 mol L^{-1} acetate buffer solution (pH 4.6), and cyclic scans were performed until no peaks came out; then the working electrode was washed with doubly distilled water and dried in air for reuse.

3 Results and discussion

3.1 Electropolymerization of crystal violet at the Gr/GCE

Crystal violet was polymerized onto the surface of the Gr/GCE by cyclic voltammetry. Polymerization parameters such polymerization potential window, scan rate, and the number of scan cycles were optimized to enhance the performance of the modified electrode. Keeping the initial polymerization potential remained at -2.0 V, Pb^{2+} and Cd^{2+} responses at the prepared PCV/Gr/GCE increased with the increasing terminal potential and reached a maximum value at about 1.8 V, after which it decreased. Therefore, the optimum terminal polymerization potential was chosen as 1.8 V. Similarly, -1.2 V was obtained as the optimum initial polymerization potential. During the polymerization, lower scan rate gives thicker polymer film as polymerization time that is longer at lower scan rate. Too thick film hinders electron transport, and too thin film gives weak catalytic activities. Experiments results show that PCV/Gr/GCE prepared at a scan rate of 80 mV s^{-1} gives the largest peak responses to both Pb^{2+} and Cd^{2+} . It was also found that the

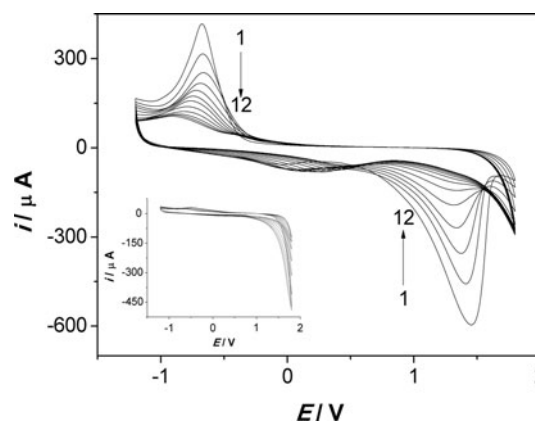


Fig. 1 Cyclic voltammograms for electropolymerization of crystal violet at a Gr/GCE in a pH 6.0 phosphate buffer containing $2.0 \times 10^{-4} \text{ mol L}^{-1}$ crystal violet. Scan rate is 80 mV s^{-1} . Inset is the cyclic voltammograms for electropolymerization of crystal violet at a bare GCE at the same polymerization conditions

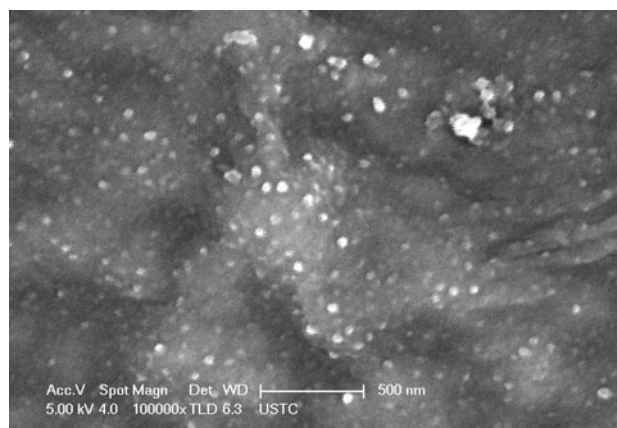


Fig. 2 SEM image of the surface of the fabricated PCV/Gr/GCE

peak responses of Pb^{2+} and Cd^{2+} increased with the number of scan cycles and reached maximum at 12 cycles and then stabilized. As a result of the optimization, the electropolymerization was carried out in a potential range of -1.2 – 1.8 V for 12 cycles at a scan rate of 80 mV s^{-1} .

Figure 1 shows the cyclic voltammograms of $2.00 \times 10^{-4} \text{ mol L}^{-1}$ crystal violet at the Gr/GCE under the above optimized polymerization conditions. From the figure, we can see that a pair of well-defined redox peaks of monomer crystal violet was observed in the first cycle, and the intensity of peaks gradually decreased as the cyclic scan continued. The decreasing redox peak currents suggested a decreasing concentration of monomer crystal violet in the solution, which reflected the continuous polymerization of crystal violet. As a result of the polymerization, a uniform adherent blue polymer film was formed at the surface of the electrode. Figure 2 shows the SEM images of the fabricated PCV/Gr/GCE. From which we can see that crystal violet has been successfully polymerized onto the graphene film of the

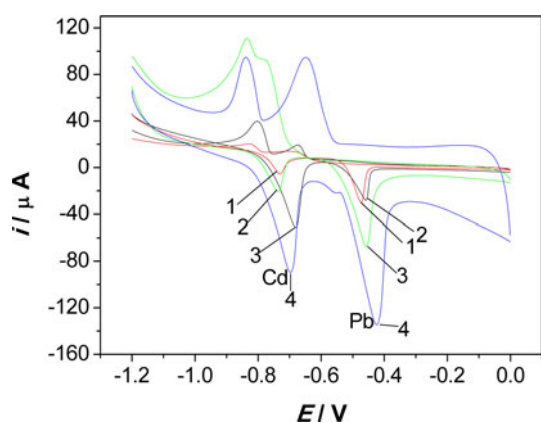


Fig. 3 Cyclic voltammograms of $2.0 \times 10^{-5} \text{ mol L}^{-1} \text{ Pb}^{2+}$ and $2.0 \times 10^{-5} \text{ mol L}^{-1} \text{ Cd}^{2+}$ at a bare GCE (1), a PCV/GCE (2), a Gr/GCE (3), and a PCV/Gr/GCE (4) in a pH 4.6 HAc–NaAc buffer. Scan rate 100 mV s^{-1}

Gr/GCE, and the polymerized poly(crystal violet) shows a flake-like structure and scatters on the graphene film.

3.2 Electrochemical behaviors of Pb^{2+} and Cd^{2+}

Figure 3 shows the cyclic voltammograms of Pb^{2+} and Cd^{2+} at the bare GCE, the PCV/GCE, the Gr/GCE, and the PCV/Gr/GCE. From the figure, we can see that only very weak oxidation peak currents of Pb^{2+} and Cd^{2+} were observed in case of using the bare GCE (curve 1, Fig. 3). At the PCV/GCE, the oxidation peak current of Pb^{2+} was greatly enhanced, and there was almost no change in the Cd^{2+} oxidation peak current (curve 2, Fig. 3). At the Gr/GCE, both the oxidation current of Pb^{2+} and the oxidation current of Cd^{2+} increased patently (curve 3, Fig. 3). While at the PCV/Gr/GCE, the oxidation peak currents of the two species were greatly increased (curve 4, Fig. 3). The catalytic effect of graphene film may be attributed to graphene's fast electron transfer property and its special chemical, and nanomesh structure resulted from its oxidation–reduction preparation process. Crystal violet can act as an efficient electron mediator, showing good electrocatalytic activities for many species in electrochemical reactions. When crystal violet is polymerized onto the graphene film deposited on the surface of an electrode, benzene rings in PCV can interact with benzene rings on planer graphene through π – π electron coupling, which strengthens the adsorption between them. The synergized effects of the PCV and the graphene make the catalysis and the electron transfer at the much more efficient.

3.3 Optimization of experimental conditions

Optimum conditions for the electrochemical response were established by measuring the peak current in dependence

on parameters such as pH of supporting electrolyte, scan rate.

3.3.1 Effect of pH of supporting electrolyte

The pH effect of acetate buffer on the oxidation current of Pb^{2+} and Cd^{2+} was studied to find out the optimum analytical pH value. Figure 4 shows the influence of the pH of acetate buffer on the oxidation peak currents of Pb^{2+} and Cd^{2+} . From the figure, we can see that, in a pH range of 2.6–5.8, the peak potentials of both Pb^{2+} and Cd^{2+} shifted negatively with increasing pH, indicating that both oxidation processes are proton-dependent. The pH change of acetate buffer exerts not much influence on the oxidation peak current of Pb^{2+} (Fig. 4a), while oxidation peak current of Cd^{2+} has a big jump at pH 4.6 (Fig. 4b), therefore, an acetate buffer of pH 4.6 was chosen as the supporting electrolyte.

3.3.2 Effect of scan rate

The effect of scan rate on the redox reaction of Pb^{2+} and Cd^{2+} at the PCV/Gr/GCE was examined in the range of 20 – 340 mV s^{-1} . Figure 5 shows the influence of scan rate on the oxidation peak currents of Pb^{2+} and Cd^{2+} . From the figure, we can see that the oxidation potentials of the two species shifted positively and their reduction potentials shifted negatively with the increase of scan rate. The oxidation peak current of Pb^{2+} increased linearly with the increasing scan rate in the range of 20 – 340 mV s^{-1} with a linear regression equation that can be expressed as $i_{\text{pa}} = 6.77 \times 10^{-5} + 5.29 \times 10^{-7}v$, $R = 0.9906$. Similarly, the oxidation peak current of Cd^{2+} increased linearly with the increasing scan rate ranging from 20 to 220 mV s^{-1} , and its linear regression equation can be expressed as $i_{\text{pa}} = 2.98 \times 10^{-5} + 5.49 \times 10^{-7}v$, $R = 0.9910$. These show that the electrochemical behaviors of both species at the PCV/Gr/GCE were adsorption processes. Experimental results also show that the limit of detection becomes lower when the scan rate is higher than 100 mV s^{-1} . Therefore, a scan rate of 100 mV s^{-1} was chosen as the optimum scan rate for the determination.

3.4 Linearity range, limit of detection and reproducibility

Under the optimized conditions, the linear range, limit of detection, and reproducibility were investigated by differential pulse voltammetry. Figure 6 shows the differential pulse voltammograms of various concentrations of Pb^{2+} and Cd^{2+} at the PCV/Gr/GCE. From the figure, we can see that the oxidation peak current of Pb^{2+} increases linearly

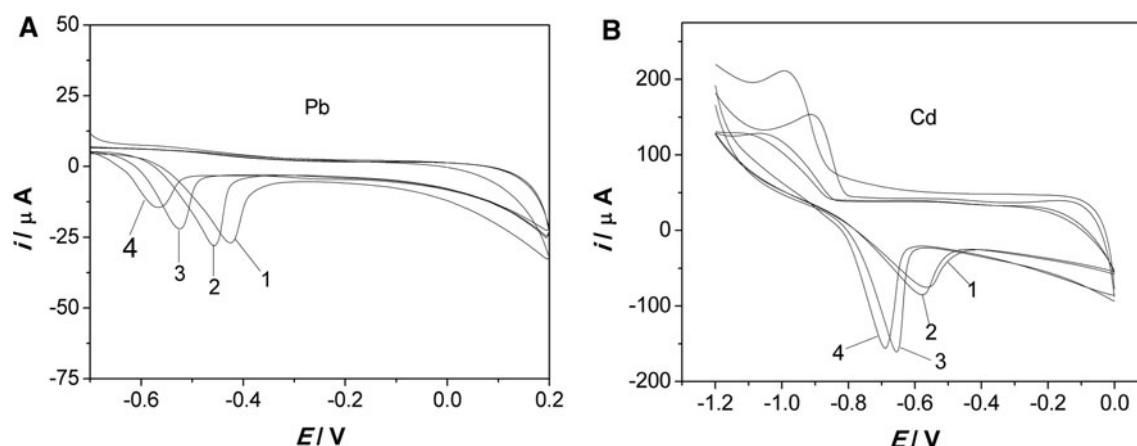


Fig. 4 Cyclic voltammograms of $1.00 \times 10^{-5} \text{ mol L}^{-1} \text{ Pb}^{2+}$ (a) and $4.00 \times 10^{-5} \text{ mol L}^{-1} \text{ Cd}^{2+}$ (b) at a PCV/Gr/GCE in acetate buffers of various pH values. Each of the numbers from 1 to 4 corresponds to a pH of 2.6, 3.8, 4.6, and 5.8, respectively. Scan rate 100 mV s^{-1}

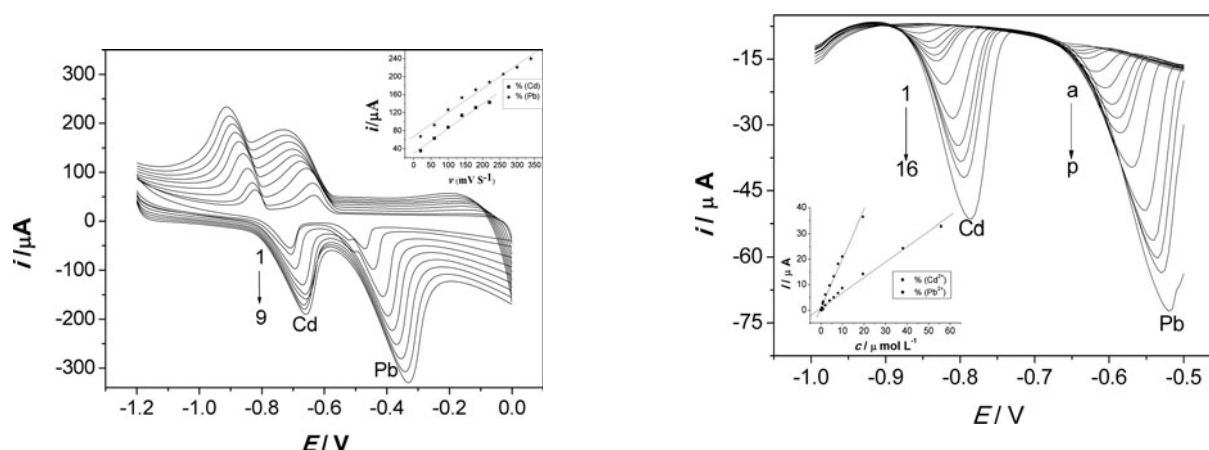


Fig. 5 Cyclic voltammograms of $1.00 \times 10^{-5} \text{ mol L}^{-1} \text{ Pb}^{2+}$ and $5.00 \times 10^{-5} \text{ mol L}^{-1} \text{ Cd}^{2+}$ at a PVC/Gr/GCE in pH 4.6 acetate buffer. Each of the numbers from 1 to 9 corresponds to a scan rate of 20, 60, 100, 140, 180, 220, 260, 300, and 340 mV s^{-1} , respectively. Inset is the plot of oxidation peak currents of Pb^{2+} and Cd^{2+} versus scan rates

with the increase of the concentration of Pb^{2+} in a ranging from 2.00×10^{-8} to $1.95 \times 10^{-5} \text{ mol L}^{-1}$, and the linear function can be expressed as $i_{\text{pa}} = 1.87C + 1.43 \times 10^{-6}$, $R = 0.9944$. The oxidation peak current of Cd^{2+} increases linearly with the increase of the concentration of Cd^{2+} in a ranging from 4.00×10^{-8} to $5.58 \times 10^{-5} \text{ mol L}^{-1}$, and the linear function can be expressed as $i_{\text{pa}} = 0.59C + 1.17 \times 10^{-6}$, $R = 0.9938$. The limits of detection for Pb^{2+} and Cd^{2+} were 6.00×10^{-9} and $1.00 \times 10^{-8} \text{ mol L}^{-1}$, respectively, defined by a signal-to-noise ratio of 3. Ten parallel measurements were made when determining $1.00 \times 10^{-5} \text{ mol L}^{-1} \text{ Pb}^{2+}$ and $1.00 \times 10^{-5} \text{ mol L}^{-1} \text{ Cd}^{2+}$ samples. The relative standard deviation was found to be less than 3.0 %, indicating good reproducibility of the method.

Fig. 6 Differential pulse voltammograms of a mixture containing Pb^{2+} and Cd^{2+} at the PVC/Gr/GCE in pH 4.6 acetate buffer. Concentrations of Pb^{2+} (from a to n): 2.00×10^{-8} , 4.00×10^{-8} , 6.00×10^{-8} , 8.00×10^{-8} , 2.00×10^{-7} , 4.00×10^{-7} , 8.00×10^{-7} , 1.00×10^{-6} , 2.00×10^{-6} , 3.98×10^{-6} , 5.95×10^{-6} , 7.92×10^{-6} , 9.87×10^{-6} and $1.95 \times 10^{-5} \text{ mol L}^{-1}$, respectively. Concentrations of Cd^{2+} (from 3 to 16): 4.00×10^{-8} , 8.00×10^{-8} , 2.00×10^{-7} , 4.00×10^{-7} , 8.00×10^{-7} , 1.00×10^{-6} , 2.00×10^{-6} , 3.98×10^{-6} , 5.95×10^{-6} , 7.92×10^{-6} , 9.87×10^{-6} , 1.95×10^{-5} , 3.81×10^{-5} and $5.58 \times 10^{-5} \text{ mol L}^{-1}$, respectively. Inset is the plot of oxidation peak currents of Pb^{2+} and Cd^{2+} versus their concentrations

3.5 Stability and reproducibility of the PCV/Gr/GCE

Stability of the PCV/Gr/GCE was evaluated by storing the electrode in air for 30 days, and then the DPVs were recorded and compared with the DPVs obtained previously. The electrode retained 99.4 and 99.2 % of their initial peak current responses for $1.00 \times 10^{-5} \text{ mol L}^{-1} \text{ Pb}^{2+}$ and $5.00 \times 10^{-5} \text{ mol L}^{-1} \text{ Cd}^{2+}$ standard solution, respectively, indicating good stability of the fabricated electrode. In order to study the reproducibility of the electrode preparation procedure, five modified electrodes based on the same procedure were fabricated and used for the determination of $1.00 \times 10^{-5} \text{ mol L}^{-1} \text{ Pb}^{2+}$ and $5.00 \times 10^{-5} \text{ mol L}^{-1} \text{ Cd}^{2+}$ standard solution. The RSD

Table 1 Comparison of the proposed method with some literature reported methods

Electrode	Detection limit	Linearity range	References
Bismuth film electrode	Pb ²⁺ : 6.9 $\mu\text{g L}^{-1}$ Cd ²⁺ : 1.4 $\mu\text{g L}^{-1}$	Pb ²⁺ : 10–100 $\mu\text{g L}^{-1}$ Pb ²⁺ : 10–100 $\mu\text{g L}^{-1}$	[31]
Nafion-coated bismuth film electrode	Pb ²⁺ : 0.07 mg L^{-1} Cd ²⁺ : 0.08 mg L^{-1}	Pb ²⁺ : 0.25–250 mg L^{-1} Cd ²⁺ : 0.5–100 mg L^{-1}	[33]
Graphene CPE	Pb ²⁺ : 0.04 $\mu\text{g L}^{-1}$ Cd ²⁺ : 0.07 $\mu\text{g L}^{-1}$	Pb ²⁺ : 0.10–50.0 $\mu\text{g L}^{-1}$ Cd ²⁺ : 0.10–50.0 $\mu\text{g L}^{-1}$	[35]
Titanium dioxide/zirconium dioxide CPE	Pb ²⁺ : 7.6 μM Cd ²⁺ : 11 μM	Pb ²⁺ : 10 mM–10 μM Cd ²⁺ : 10 mM–50 μM	[36]
Ion exchange synthetic resin-modified carbon nanotube paste electrode	Pb ²⁺ : 12 nM Cd ²⁺ : 20 nM	Pb ²⁺ : 0.01–58.0 μM Cd ²⁺ : 0.7–25.0 μM	[37]
Montmorillonite-calcium-modified CPE	Pb ²⁺ : 0.30 $\mu\text{g L}^{-1}$ Cd ²⁺ : 0.54 $\mu\text{g L}^{-1}$	Pb ²⁺ : 1.0–100.0 $\mu\text{g L}^{-1}$ Cd ²⁺ : 1.8–120.0 $\mu\text{g L}^{-1}$	[39]
Polyaniline-modified GCE	Pb ²⁺ : 0.1 μM Cd ²⁺ : 0.13 μM	Pb ²⁺ : 0–2 μM Cd ²⁺ : 0–2 μM	[40]
PMC/Gr/GCE	Pb ²⁺ : 6.00 nM Cd ²⁺ : 10.0 nM	Pb ²⁺ : 0.020–19.5 μM Cd ²⁺ : 0.040–55.8 μM	This work

for the between electrode peak currents (average of six determinations on each electrode) was calculated to be 3.5 %, indicating good reproducibility of the electrode preparation procedure.

3.6 Interference studies

The influence of some other common metal ions on the determination of $1.00 \times 10^{-5} \text{ mol L}^{-1} \text{ Pb}^{2+}$ and $5.00 \times 10^{-5} \text{ mol L}^{-1} \text{ Cd}^{2+}$ was investigated. If peak current change is no more than $\pm 5 \%$ when measurements were conducted in the absence and presence of a foreign species, then we assume no interference occurs. Experimental results indicated that no interference was observed when determinations were carried out in the presence of K^+ (1000), Na^+ (1000), Ca^{2+} (1000), NH_4^+ (1000), Al^{3+} (500), Mn^{2+} (100), Ni^{2+} (100), NO_3^- (500), and Cl^- (500), indicating that the PCV/Gr/GCE is highly selective toward the determination of Pb^{2+} and Cd^{2+} , where the data in the parenthesis are the concentration ratios of those interferents to Pb^{2+} and Cd^{2+} . These results indicated good selectivity of the method for the determination of Pb^{2+} and Cd^{2+} .

3.7 Comparison of the proposed method with some literature reported electrochemical methods

Table 1 shows the comparison between the analytical performance of the proposed method and some previous electrochemical methods for the determination of Pb^{2+} and Cd^{2+} . It can be seen from the table that the proposed method is better or comparable to these previous reported methods in terms of detection limit and linearity range.

3.8 Application

The practical application of the PCV/Gr/GCE was evaluated using river water samples. Water samples collected from Zhaowang river, Wanfu river, and Leize lake were analyzed in accordance with procedures described in the experimental section. No peak currents of Pb^{2+} and Cd^{2+} were observed in the voltammograms of these samples, indicating that no Pb^{2+} and Cd^{2+} are contained in these samples, or the concentration is lower than their limit of detection. The sensitivity of this method is not enough for detecting Pb^{2+} and Cd^{2+} content in these real samples. Then the samples were spiked with a series of Pb^{2+} and Cd^{2+} standard solutions and similarly analyzed. The results and the calculated recoveries and RSD of the analysis are shown in Table 2.

4 Conclusions

In this study, a novel poly(crystal violet)/graphene composite electrode was fabricated using a two-step procedure by electropolymerizing crystal violet onto the surface of a graphene-modified electrode, which is obtained by casting a certain amount of well-dispersed graphene suspension onto a prior polished glassy carbon electrode. Utilizing the PCV/Gr/GCE, an electrochemical sensor for the simultaneous determination of Pb^{2+} and Cd^{2+} in aqueous solution was developed. Experimental results show that the modified electrode exhibited excellent electrocatalytic activity toward the electrochemical oxidation of Pb^{2+} and Cd^{2+} . In a pH 4.6 acetate buffer solution, the oxidation peak current of Pb^{2+} and Cd^{2+}

Table 2 Determination results of Pb²⁺ and Cd²⁺ in water samples (*n* = 6)

Samples	Spiked (mol L ⁻¹)	Found (mol L ⁻¹)		Recovery (%)		RSD (%)	
		Pb ²⁺	Cd ²⁺	Pb ²⁺	Cd ²⁺	Pb ²⁺	Cd ²⁺
Water from Zhaowang river	0.00	ND	ND	ND	ND	ND	ND
	6.00×10^{-7}	5.98×10^{-7}	5.86×10^{-7}	99.7	97.7	3.51	3.84
	1.00×10^{-6}	1.01×10^{-6}	9.99×10^{-7}	101	99.9	3.64	3.47
	1.00×10^{-5}	9.75×10^{-6}	9.69×10^{-6}	97.5	96.9	2.24	3.41
Water from Wanfu river	0.00	ND	ND	ND	ND	ND	ND
	6.00×10^{-7}	5.91×10^{-7}	5.76×10^{-7}	98.5	96.0	4.51	4.74
	1.00×10^{-6}	9.94×10^{-7}	9.88×10^{-7}	99.4	98.8	3.54	3.86
	1.00×10^{-5}	9.89×10^{-6}	9.66×10^{-6}	98.9	96.6	3.24	3.64
Water from Leize lake	0.00	ND	ND	ND	ND	ND	ND
	6.00×10^{-7}	5.78×10^{-7}	5.91×10^{-7}	96.3	98.5	3.21	3.54
	1.00×10^{-6}	9.57×10^{-6}	9.57×10^{-7}	95.7	97.8	3.14	3.27
	1.00×10^{-5}	9.94×10^{-6}	9.68×10^{-6}	99.4	96.8	2.84	3.01

obtained by DPV was linearly proportional to their corresponding concentrations in the ranges of 2.00×10^{-8} – 1.95×10^{-5} and 4.00×10^{-8} – 5.58×10^{-5} mol L⁻¹, respectively. The detection limits for Pb²⁺ and Cd²⁺ were estimated to be 6.00×10^{-9} and 1.00×10^{-8} mol L⁻¹, respectively. The modified electrode shows excellent selectivity and reproducibility for the voltammetric determination of Pb²⁺ and Cd²⁺ and has been successfully applied for the determination of Pb²⁺ and Cd²⁺ in water samples.

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